

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 July 2003 (31.07.2003)

PCT

(10) International Publication Number  
**WO 03/062305 A1**

- (51) International Patent Classification<sup>7</sup>: C08G 73/02, H01B 1/12 (74) Agent: MURCITROYD & COMPANY; Scotland House, 165-169 Scotland Street, Glasgow G5 8PL (GB).
- (21) International Application Number: PCT/GB03/00254 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 24 January 2003 (24.01.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0201593.1 24 January 2002 (24.01.2002) GB (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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- Published:**  
— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 03/062305 A1

(54) Title: FERROMAGNET

(57) Abstract: Described is a ferromagnetic material comprising a substituted conjugated polymer which comprises a conjugated polymer which is substituted with an organic electron acceptor. The material is preferably ferromagnetic at room temperature (290K) and, most preferably, is ferromagnetic at temperatures above room temperature. In a preferred embodiment, the conjugated polymer is polyaniline and the electron acceptor is tetracyanoquinodimethane (TCNQ). Also described is a method for producing the substituted conjugated polymer and uses of the material.

1 "Ferromagnet"

2

3 This invention relates to a room temperature  
4 ferromagnetic non-metallic material and, in  
5 particular, to a room temperature ferromagnetic  
6 polymer.

7

8 In recent years there has been a large interest in  
9 the formation of new magnetic materials from non-  
10 metallic molecules. So far polymers have failed to  
11 make an impact in this area, mainly because of the  
12 difficulties posed in the production of highly  
13 ordered or even crystalline polymers. Such  
14 structural order is required to observe magnetic  
15 effects.

16

17 In particular, there has been little progress in the  
18 formation of non-metallic ferromagnetic materials.  
19 Ferromagnetic materials have many applications e.g.,  
20 for electromagnets, transformers, magnetic tape  
21 recording, magnetic shielding, magneto-optical data  
22 storage and magnetic transistors. Almost all known

1 ferromagnetic materials are metallic in nature. As  
2 such their production may attract processing  
3 difficulties, for example, due to the heaviness of  
4 the material, and they may be expensive to produce.  
5  
6 A problem associated with the production of a non-  
7 metallic ferromagnetic material is that of  
8 synthesising molecules which have a high enough  
9 density of localised spins which are physically  
10 close enough in space to yield a high enough  
11 exchange interaction for the material to exhibit  
12 ferromagnetism. The molecules in a ferromagnetic  
13 material need to be positioned so that the weak  
14 exchange interactions between each spin give rise to  
15 ferromagnetic ordering. This is difficult to  
16 achieve and, in almost all cases, it is found that  
17 the exchange interaction is so weak that a  
18 ferromagnetic phase is only observed at low  
19 temperatures such as 2-4 K. Difficulties can arise  
20 in the preparation of non-metallic ferromagnetic  
21 materials, for example, when radicals are generated  
22 by oxidation. In these cases it is difficult to  
23 maintain a high packing density and degree of order,  
24 whilst permitting access of the oxidising agents  
25 into the structure to form the radicals.  
26  
27 It follows that another problem associated with the  
28 production of non-metallic ferromagnetic materials  
29 is that of producing a material which is  
30 ferromagnetic at room temperature (i.e. 290 K) or  
31 higher, i.e. has a Curie temperature ( $T_c$ ) of greater  
32 than or equal to room temperature. Clearly this has

1     implications for the end use of the material. To  
2     date, there has been only one report of room  
3     temperature ferromagnetic non-metallic material  
4     (Markarova T. L. et al, Magnetic Carbon, Nature,  
5     413, 716-718 (2001) reported a weakly ferromagnetic  
6     phase in  $C_{60}$  at room temperature). However, the  
7     results of this report are clearly non-reproducible.

8  
9     It is therefore an aim to provide a ferromagnetic  
10    non-metallic material. In particular, it is an aim  
11    to provide a non-metallic material that is  
12    ferromagnetic at room temperature.

13  
14    The present invention provides a substituted  
15    conjugated polymer comprising a conjugated polymer  
16    which is substituted with an organic electron  
17    acceptor.

18  
19    In particular the present invention provides a  
20    ferromagnetic material comprising a conjugated  
21    polymer which is substituted with an organic  
22    electron acceptor. The material is ferromagnetic at  
23    temperatures above 200K, preferably ferromagnetic at  
24    temperatures above 250K, more preferably  
25    ferromagnetic at room temperature (290K) and, most  
26    preferably, is ferromagnetic at temperatures above  
27    room temperature. In a particularly preferred  
28    embodiment, the material of the present invention is  
29    ferromagnetic up to 400K, more preferably up to  
30    500K. The material has a mass magnetisation at room  
31    temperature of at least  $0.003 \text{ JT}^{-1}\text{Kg}^{-1}$ . More  
32    preferably, it has a mass magnetisation at room

1 temperature of between  $0.003$  and  $10 \text{ JT}^{-1}\text{Kg}^{-1}$ , more  
2 preferably between  $0.003$  and  $20 \text{ JT}^{-1}\text{Kg}^{-1}$ , most  
3 preferably between  $0.003$  and  $30 \text{ JT}^{-1}\text{Kg}^{-1}$ .  
4

5 By conjugated polymer is meant that the polymer  
6 comprises alternating single and double bonds  
7 between carbon atoms so that a  $\pi$  electron system is  
8 formed along the polymer chain. Preferably the  
9 conjugated polymer comprises aromatic groups. These  
10 aromatic groups may be heterocyclic aromatic groups  
11 and in a preferred embodiment the heterocyclic  
12 aromatic groups contain a nitrogen atom in the ring  
13 structure. Examples of suitable conjugated polymers  
14 are polyaniline, polypyridine, polypyrrole,  
15 polyparaphenylene, polyphenylene-vinylene (PPV),  
16 polythiophene or polyfluorene. The conjugated  
17 polymer can be a polymer obtainable by polymerising  
18 substituted monomers of aniline, pyridine, pyrrole,  
19 phenylene, phenylene-vinylene, thiophene or  
20 fluorene. For example, poly(2-methoxy,5-(2'-ethyl-  
21 hexyloxy)-p-phenylenevinylene (MEH-PPV) is a  
22 suitable conjugated polymer obtainable by  
23 polymerising substituted phenylene-vinylene  
24 monomers.  
25

26 In a preferred embodiment the conjugated polymer is  
27 polyaniline or is a polymer obtained from  
28 substituted aniline monomers. The term polyaniline  
29 includes all different forms of polyaniline (leuco-  
30 emeraldine base, emeraldine base and  
31 pernigraniline). Emeraldine base polyaniline is  
32 particularly preferred. The emeraldine base


1 polyaniline is prepared by the method outlined by  
2 A.P. Monkman et al in Low Temperature Synthesis of  
3 High Molecular weight Polyaniline, Polymer, 37,  
4 3411-3417 (1996).

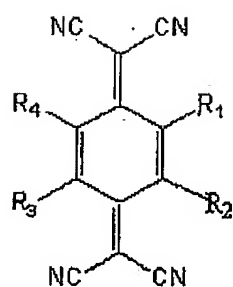
5  
6 The conjugated polymer preferably has a number  
7 average molecular weight of greater than 4000 and  
8 more preferably greater than 19000 Dalton.  
9 Typically the number average molecular weight is in  
10 the range of 4000 to 250 000 Dalton.

11  
12 The organic electron acceptor forms a charge  
13 transfer complex with the conjugated polymer.  
14 Preferably the organic electron acceptor readily  
15 forms radicals.

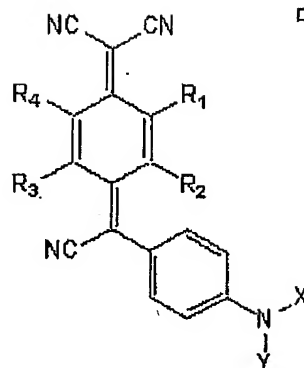
16  
17 The organic electron acceptor may be chosen from:  
18 tetracyanoquinodimethane (TCNQ);  
19 tetracyanonaphthoquinodimethane (TNAP);  
20 tetracyanoethylene (TCNE);  
21 dichlorodicyanobenzoquinone (DDQ); TCNQ derivatives;  
22 or other such electron acceptors.

23  
24 The family of TCNQ derivatives includes, but is not  
25 limited to, the following:

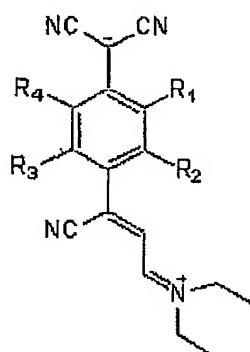




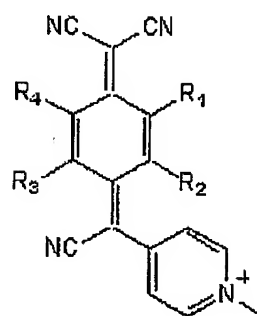
Formula I



Formula II



Formula III

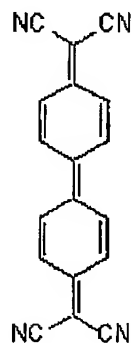


Formula IV

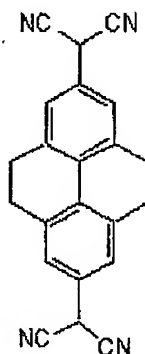
- 1 where
- 2  $R_1 = R_2 = R_3 = R_4 = \text{F, Me, Ph or NCHCHN}$ ; or
- 3  $R_2 = R_4 = \text{H}$  and  $R_1 = R_3 = \text{I, Br, OMe, CN, PhCH}_2$ , a  $\text{C}_1\text{-C}_8$
- 4 alkyl group (preferably hexyl, Me, Et or iPr); or
- 5  $R_2 = R_4 = \text{H}$  and  $R_1 = \text{OMe}$  and  $R_3 = \text{OEt, OiPr, OiButyl,}$
- 6  $\text{OiPentyl}$ ; or

- 1  $R_2 = R_4 = H$  and  $R_1 = OEt$  and  $R_3 = SMe$ ; or  
 2  $R_2 = R_4 = H$  and  $R_3 = Me$  and  $R_1 = I, Br$  or  $Cl$ ; or  
 3  $R_1 = R_2 = OCH_2CH_2O$  and  $R_3 = OMe$  and  $R_4 = H$ ; or  
 4  $R_2 = R_4 = H$  and  $R_3 = Br$  and  $R_1 = OCH_2CH_2OH$ ; or  
 5  $R_2 = R_3 = R_4 = H$  and  $R_1 = Me, Et, OMe, CO_2Me, ;$  and  
 6  $X = Y = C_1-C_8$  alkyl group or  $CH_2CH_2OH$ ; or  $X = C_1-C_8$   
 7 alkyl group and  $Y = CH_2CH_2OH$

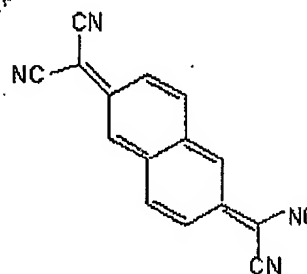
8  
 9 The following structures are also included within  
 10 TCNQ derivatives:



Formula V



Formula VI



Formula VII

11 In preferred embodiments of the invention, the  
 12 organic electron acceptor is preferably  
 13 tetracyanoquinodimethane (TCNQ). This is a stable  
 14 radical forming molecule which readily forms charge  
 15 transfer complexes with electron donors such as  
 16 nitrogen atoms on a heterocyclic conjugated polymer  
 17 having nitrogen in its ring structure.

18



1 It is believed that the mass magnetisation of the  
2 material depends on the degree of substitution of  
3 the polymer backbone with the organic electron  
4 acceptors. Preferably the degree of substitution is  
5 such that the ferromagnetic material has a mass  
6 magnetisation at room temperature of at least 0.003  
7  $\text{JT}^{-1}\text{Kg}^{-1}$ .

8  
9 The present invention also provides a method for  
10 producing a ferromagnetic polymer which method  
11 comprises reacting a conjugated polymer with an  
12 organic electron acceptor.

13  
14 In a preferred embodiment the method comprises the  
15 following steps:

- 16  
17 a) dissolving the conjugated polymer in an  
18 appropriate solvent,  
19  
20 b) adding the organic electron acceptor to the  
21 solution and refluxing the resultant solution for at  
22 least 24 hours,  
23  
24 c) cooling and filtering the refluxed solution  
25 from step b and collecting and evaporating the  
26 filtrate to form a solid polymer,  
27  
28 d) drying the polymer from step c, and allowing  
29 the polymer to reach a steady ferromagnetic state.

30  
31 Typically, the conjugated polymer is dissolved in an  
32 appropriate solvent, e.g. n-methyl-2-pyrrolidinone

1 (NMP). The organic electron acceptor is added to  
2 the solution and the mixture is refluxed for at  
3 least 24 hours. Typically the molar ratio of  
4 polymer and organic electron acceptor in the mixture  
5 is 1:2. The solution is then cooled and filtered.  
6 The filtrate is collected and evaporated to form a  
7 solid polymer. This polymer is then dried under  
8 vacuum at 80°C. The polymer is then left until it  
9 reaches a steady ferromagnetic state. Typically  
10 this will take any time up to 4 weeks. Preferably  
11 the polymer remains in a vacuum or in an inert  
12 atmosphere during this step.

13  
14 In a particularly preferred embodiment the  
15 conjugated polymer is the emeraldine base form of  
16 polyaniline and the organic electron acceptor is  
17 TCNQ. The resultant substituted conjugated polymer  
18 is polyaniline tricyanoquinonedimethane (PANiCNQ).  
19 Not wishing to be bound by any theory, it is  
20 believed that PANiCNQ contains stable radicals which  
21 are generated by charge transfer from the TCNQ to  
22 the amine sites on the conjugated polymer and by  
23 protonation of the imine sites on the conjugated  
24 polymer.  $\pi$ -stacking of neighbouring chains may occur  
25 and may result in interchain spacing of  
26 approximately 4 Angstrom or less. This gives rise  
27 to exchange interactions between neighbouring chains  
28 and hence a three dimensional ferromagnetic exchange  
29 mechanism in an organic system.

30  
31 Clearly the polymer of the present invention solves  
32 the problems of the prior art. However, as well as

1     having a  $T_c$  greater than or equal to room  
2     temperature, the polymer is soluble and is easily  
3     processed. For example, it is relatively easy to  
4     cast films of the polymer and spin fibres from it.  
5     The polymer of the present invention may be used as  
6     a ferromagnetic material in typical ferromagnetic  
7     applications such as low weight permanent magnets,  
8     organic motors and dynamos and magnetic shielding.  
9     It is particularly suitable for use as thin film  
10    magneto-optic data storage, magnetic security tags,  
11    magnetic shielding, magnetic sensors, magnetic  
12    transistors and signal processors.

13  
14    Indeed, further aspects of the invention include  
15    thin film magneto-optic data storage comprising a  
16    substituted copolymer or ferromagnetic material of  
17    the invention; a magnetic security tag comprising a  
18    substituted copolymer or ferromagnetic material of  
19    the invention; magnetic shielding comprising a  
20    substituted copolymer or ferromagnetic material of  
21    the invention; a magnetic sensor comprising a  
22    substituted copolymer or ferromagnetic material of  
23    the invention; a magnetic transistor comprising a  
24    substituted copolymer or ferromagnetic material of  
25    the invention; and a signal processor comprising a  
26    substituted copolymer or ferromagnetic material of  
27    the invention.

28

29    The invention is exemplified with reference to the  
30    following non-limiting description and the  
31    accompanying figures in which:

32

1 Figure 1 shows the chemical structures of TCNQ and  
2 the emeraldine base form of polyaniline along with a  
3 suggested structure of the ferromagnetic polymer  
4 (PANiCNQ) formed by substituting the emeraldine base  
5 form of polyaniline with TCNQ.

6

7 Figure 2 shows the optical (UV) spectra of as  
8 synthesised PANiCNQ.

9

10 Figure 3 shows the saturation magnetisation curve  
11 for PANiCNQ measured at room temperature. The inset  
12 depicts the temperature dependence of the  
13 magnetisation between 77 and 300K.

14

15 Figure 4a-d shows alternant images of PANiCNQ  
16 obtained using an AFM and MFM microscope. Left-hand  
17 images are AFM images and right hand images are MFM  
18 images.

19

20 Figure 4a shows the initial image of a sample from  
21 3b\_2, showing the AFM image on the left and the MFM  
22 on the right. The MFM is in phase mode.

23 Figure 4b shows that although the AFM image on the  
24 left did not change from that of Figure 4a, in the,  
25 a striation is seen moving across the MFM image from  
26 right to left.

27

28 Figure 4c, shows the striation can again be clearly  
29 seen moving across the image in the MFM mode.

30 Figure 4d shows that the MFM image changed again,  
31 indicating the presence of a magnetic domain.

32

1 Figure 5 shows the calculated moment from the  
2 contaminants of pure Pani and the actual measured  
3 moment of 13 samples.

4  
5 Figure 6 illustrates low Field ESR data for sample  
6 3b\_2 showing insulating behaviour.

7  
8 **Example 1**

9 **Preparation of polymer**

10

11 The emeraldine base form of polyaniline was  
12 prepared by the method outlined by A.P. Monkman et  
13 al in Low Temperature Synthesis of High Molecular  
14 weight Polyaniline, Polymer, 37, 3411-3417 (1996).  
15 0.5 g of it was dissolved in 100 ml of n-methyl-2-  
16 pyrrolidinone (NMP). 1.1g of TCNQ (Lancaster) was  
17 added and the solution was refluxed for  
18 approximately 24 hours. The solution was then  
19 cooled and filtered through a filter paper. The  
20 filtered solution was collected and evaporated to  
21 give a dark green/black tar polymer. The dark  
22 green/black tar polymer was dried under vacuum at 80  
23 °C. It was found that the resultant black polymer  
24 absorbs moisture on standing in air.

25

26 **Example 2**

27 **Characterisation of the polymer using Ultraviolet**  
28 **(UV) Spectroscopy.**

29

30 0.5g of the emeraldine base form of polyaniline was  
31 dissolved in 100 ml of n-methyl-2-pyrrolidinone  
32 (NMP). 2.3 g of TCNQ was added. This forms a blue

1 solution and upon refluxing as in Example 1, the  
2 solution turned dark red/black and exhibited a  
3 strong absorption band at  $\lambda_{\text{max}} = 492 \text{ nm}$  (see the  
4 solid line spectrum in Figure 2). The solvent was  
5 evaporated off under vacuum and the remaining solid  
6 was dried at  $60^\circ\text{C}$  at  $0.1 \text{ mmHg}$ . This yielded a dark  
7 green/black polymer which is also readily soluble in  
8 NMP. When dissolved in NMP this polymer gives an  
9 intense green solution. The UV absorption spectrum  
10 of this green solution indicates that a charge  
11 transfer has occurred between the TCNQ and the  
12 polyaniline, forming stable radicals on both. The  
13 UV absorption spectrum shows new absorption maxima  
14 at  $625 \text{ nm}$  and  $661 \text{ nm}$  with a weaker band at  $492 \text{ nm}$   
15 (see dashed line in Figure 2). It would appear that  
16 the charge transfer and spin separation occurs in  
17 the solid state and does not occur in solution.

18

19 **Example 3**

20 Characterisation of the polymer using Fourier  
21 Transform Infra Red (FTIR) Spectroscopy.

22

23 A sample of the polymer (PANiCNQ) produced in  
24 Example 1 was analysed using FTIR spectroscopy. The  
25 FTIR spectrum of this new polymer shows the  
26 development of a broad and strong absorption at  $2185$   
27  $\text{cm}^{-1}$  which is ascribed to TCNQ having covalently  
28 bonded to the polymer. It is believed that this  
29 bonding takes place at the amine sites along  
30 the polyaniline backbone and that the TCNQ has  
31 become a substituted side group along the conjugated  
32 backbone. Once formed, this new polymer is still

1 soluble in NMP and it is believed that charge  
2 transfer between the side groups and the backbone  
3 occurs once the solvent is removed. In this post-  
4 charge transfer state, strong broad absorption  
5 between  $2600\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$  is observed,  
6 indicative of positively charged nitrogen sites.  
7 Also observed is a strong band at  $1283\text{ cm}^{-1}$ . This is  
8 highly characteristic of CN stretches associated  
9 with semiquinoid structures in protonated  
10 polyaniline and is highly suggestive that in  
11 PANiCNQ, the quinoid imine sites are partially  
12 protonated as quinoid peaks at  $1508\text{ cm}^{-1}$  and  $1577\text{ cm}^{-1}$   
13 are still observed. It is believed that this  
14 protonation occurs during synthesis as a result of  
15 hydrogen cyanide which is given off during the  
16 attachment of the TCNQ to the polymer chain. This  
17 acid will readily protonate any imine sites. As the  
18 polymer is hygroscopic, a small broad moisture peak  
19 is also present at  $3396\text{ cm}^{-1}$ .

20

21 From this infra-red data and previous known  
22 reactions between TCNQ and amines a tentative  
23 structure for PANiCNQ is given in Figure 1. It is  
24 possible for the TCNQ to react at the meta or ortho  
25 sites on the benzene rings along the polyaniline  
26 backbone. Further, as the synthesis of this new  
27 polymer is not well characterised, it must be  
28 assumed that both incomplete TCNQ addition and  
29 protonation can take place which will give rise to  
30 variable physical properties.

31

1     **Example 4**

2     Characterisation of the polymer using X-ray  
3     Spectroscopy.

4  
5     A sample of the polymer (PANiCNQ) produced in  
6     Example 1 was analysed using X-ray spectroscopy. X-  
7     ray analysis of the dark green/black polymer  
8     revealed the polymer to be amorphous, as would be  
9     pure polyaniline.

10

11    **Example 5**

12    Magnetisation Measurements

13    To test if the new polymer had a large number of  
14    localised spins, magnetisation measurements were  
15    made on solid at room temperature using a Vibrating  
16    Sample Magnetometer (VSM) that has a sensitivity of  
17     $10^{-7}$  JT<sup>-1</sup>. A first batch of PANiCNQ was made  
18    according to the procedure of Example 1 except that  
19    the first batch did not undergo the reflux step and  
20    instead was just heated for 10 minutes. Three  
21    further batches were made according to the procedure  
22    of Example 1. In the first batch of PANiCNQ a weak  
23    signal was detected just above the background  
24    diamagnetic response. In the three subsequent  
25    batches, the reaction time was increased and more  
26    attention was paid to the stoichiometric amounts of  
27    TCNQ added to the reaction solution, the amount of  
28    TCNQ added was increased from 1 mol to 2 mols.  
29    Figure 3 shows the saturation magnetisation curve  
30    for a sample of one of the latter batches of  
31    PANiCNQ. The sample has a mass magnetisation of  
32    0.003 JT<sup>-1</sup>Kg<sup>-1</sup>. Larger magnetisation was observed



1 for this sample than for the first batch sample. The  
2 inset in Figure 3 depicts the temperature dependence  
3 of the magnetisation between 77 K and 300 K. No  
4 change in the saturation magnetisation is observed  
5 in the temperature range indicating that  $T_c$  must lie  
6 above room temperature for this material.

7  
8 The latter batches also revealed much stronger FTIR  
9 bands at  $2185\text{ cm}^{-1}$ , and a greater degree of charge  
10 transfer as seen in absorption spectra than the  
11 first batch polymer. Magnetisation measurements on  
12 these latter polymers revealed much larger  
13 magnetisation, with magnetisation saturation being  
14 easily observed at room temperature. These indicate  
15 a correlation between the degree of TCNQ  
16 substitution, charge transfer and mass  
17 magnetisation.

18  
19 From Figure 3 it is clear that there is a large  
20 ferromagnetic component imposed upon a diamagnetic  
21 background. Measurements with different samples  
22 from one of the latter batches lead to the  
23 conclusion that not all the emeraldine base had  
24 reacted to form PANiCNQ, and as polyaniline is  
25 diamagnetic this accounts for the background.

26  
27 The mass magnetisation at room temperature for the  
28 sample of Figure 3 is approximately  $0.003\text{ JT}^{-1}\text{Kg}^{-1}$ .  
29 For reference Ni has a mass magnetisation of  $55.4$   
30  $\text{JT}^{-1}\text{Kg}^{-1}$ . From the saturation magnetisation curves it  
31 is clear that the new material is ferromagnetic at  
32 room temperature. Further simple evidence of this is

1 the fact that lumps of the polymer can be picked up  
2 with a small permanent magnet.

3

#### 4 Example 6

##### 5 Thermal Analysis

6

7 A sample of PANiCNQ was prepared in accordance with  
8 the procedure of Example 1. The sample observed  
9 whilst it was heated at a rate of 1°C/min. The  
10 thermal analysis of PANiCNQ indicated that the  
11 polymer is stable up to and even beyond 500° C.  
12 This is characteristic of the emeraldine form of  
13 polyaniline. A possible weak glass transition is  
14 seen at 260° C.

15

#### 16 Example 7

##### 17 Impurity analysis

18

19 FTIR spectroscopy of the new material was made to  
20 determine the degree of magnetic impurity. A sample  
21 of PANiCNQ was prepared in accordance with the  
22 procedure of Example 1. According to spectroscopy  
23 measurements less than 50 ppm of the sample is iron.  
24 Therefore calculations were carried out on the  
25 assumption that the iron would form in the system as  
26 a cluster, and thus have the most effect upon the  
27 magnetisation. Even then the maximum magnetic moment  
28 calculated was of the order  $10^{-10}$  JT<sup>-1</sup>. The mass  
29 magnetisation equipment used in these experiments  
30 has a sensitivity of approximately  $10^{-7}$  JT<sup>-1</sup>. Thus  
31 impurities cannot account for the signal measured in  
32 the polymer. In addition to this, the first batch

1 of polymer which showed a weak ferromagnetic signal  
2 was retested a month later. The sample had been  
3 left in its test capsule in a sealed glass bottle.  
4 The ferromagnetic signal had increased dramatically  
5 during this time, indicating clearly that the  
6 magnetism emanates from the sample and that the  
7 solid state reaction must involve a spin separation  
8 step which is rather a slow process.

9

#### 10 Example 8

#### 11 Analysis of Polymer Using AFM and MFM

12

13 PANiCQ was prepared as described above and samples  
14 analysed using an atomic force microscope (AFM) and  
15 a magnetic force microscope (MFM). The images were  
16 taken from batch number three. Samples were chosen  
17 due to their physical size and smoothness. The  
18 experiment was carried out upon a digital  
19 instruments AFM/MFM at Florida State University.  
20 Images obtained using the microscopes are shown in  
21 Figures 4a- 4d, with the left hand images showing  
22 AFM images obtained and the right hand images  
23 showing MFM images. The images are alternant from  
24 AFM to MFM respectively as this is necessary to  
25 prove that changes in the MFM image are not  
26 structural.

27

28 Figure 4a shows the initial image of a sample from  
29 3b\_2, showing the AFM image on the left and the MFM  
30 on the right. The MFM is in phase mode.

31

1 Figure 4b shows that the AFM image on the left did  
2 not change from that of Figure 4a. However in the  
3 MFM image, a striation is seen moving across the  
4 image right to left. The MFM is in phase mode.

5

6 In Figure 4c, the striation can again be clearly  
7 seen moving across the image in the MFM mode.

8

9 Fig 4d shows that the MFM image changed again,  
10 indicating the presence of a magnetic domain.

11

12 The sample examined in Figure 4 was individually run  
13 upon an Alternating Gradient Field Magnetometer  
14 (AGFM). The inventors noted what appeared to be weak  
15 hysteretic behaviour. The data followed a similar  
16 trend to all the other data with weak ferromagnetic  
17 behaviour upon a diamagnetic background. Without  
18 being limited, the inventors expect the magnetism to  
19 be most prevalent at the sample surface due to the  
20 requirement that the quinoid ring has to be  
21 activated. The polymer may even benefit from  
22 crushing as the size of the polymer is not  
23 important. The hard magnetic properties may be  
24 affected as one possibly will break down the inter-  
25 chain exchange

26

27 Similar images were obtained using other smaller  
28 crystalline regions within the sample (data not  
29 shown).

30

31 Example 9

32 Testing of Base Materials For Contamination

1 The base materials were tested for contamination on  
2 the Vibrating Sample Magnetometer (VSM) in order to  
3 discount the possibility of dirt in the sample. The  
4 absolute measurement was not the moment of the  
5 sample but the mass magnetisation when comparing  
6 results. However for simplicity's sake Figure 5  
7 shows the moment of the sample and contaminants. Fig  
8 5 shows the measured moment against the calculated  
9 moment for all the possible contaminants of Pani  
10 (polyaniline).

11

12 As shown in Figure 5, the measured moment is an  
13 order of magnitude less than the calculated moment.  
14 Table 1 shows the contamination levels of the  
15 transition metals. The table shows the calculated  
16 contamination of the transition metals compared to  
17 the actual measured moment of the relevant sample.  
18 According to the mass spectroscopy there was no Co  
19 in any of the samples.

Table 1

Pure Pani sample	Calculated Ni Contamination From mass spec (J/T)	Calculated Fe Contamination From mass spec (J/T)	Measured Moment (J/T)
1	$3 \times 10^{-8}$	$4 \times 10^{-7}$	$4 \times 10^{-8}$
2	$2 \times 10^{-8}$	$3.27 \times 10^{-7}$	$3.5 \times 10^{-8}$
3	$1.5 \times 10^{-8}$	$1.172 \times 10^{-6}$	$1.5 \times 10^{-8}$
4	$1.1 \times 10^{-8}$	$1.19 \times 10^{-7}$	$3 \times 10^{-8}$
5	$1.5 \times 10^{-8}$	$5.9 \times 10^{-8}$	$1 \times 10^{-8}$
6	$1 \times 10^{-8}$	$1.5 \times 10^{-7}$	$1.3 \times 10^{-8}$
7	$7 \times 10^{-9}$	$1.75 \times 10^{-7}$	$1.2 \times 10^{-8}$
8	$8 \times 10^{-9}$	$6.5 \times 10^{-8}$	$1.1 \times 10^{-8}$
9	$1. \times 10^{-8}$	$1 \times 10^{-7}$	$4 \times 10^{-9}$
10	$1.3 \times 10^{-8}$	$7.9 \times 10^{-8}$	$6 \times 10^{-9}$
11	$6 \times 10^{-9}$	$4.5 \times 10^{-8}$	$1.7 \times 10^{-8}$
12	$1.5 \times 10^{-8}$	$1.26 \times 10^{-7}$	$2.44 \times 10^{-8}$
13	$1.2 \times 10^{-8}$	$1.47 \times 10^{-7}$	$2.3 \times 10^{-8}$

1 From the table, it is clear that the Ni is  
 2 approximately of the right level and, apart from the  
 3 spurious result, the levels of transition metals are  
 4 within the experimental errors. Accordingly the  
 5 inventors believe that the Fe content obtained via  
 6 mass spectroscopy may be an over estimate due to the  
 7 fact that ArO has an identical mass to Fe. Hence  
 8 when examining PANiCNQ, Ni is the only real  
 9 transition element of interest. It is however once  
 10 again worth explicitly stating that even if one  
 11 includes all the contaminants it does not account  
 12 for all the magnetism seen in this sample.  
 13

1 The other base materials of the sample, TCNQ and  
2 NMP, are diamagnetic, and were found to be  
3 essentially pure as no contaminants can be seen with  
4 the VSM.

5

#### 6 **Example 10**

#### 7 **ESR Measurements of Polymer**

8

9 Electron Spin Resonance (ESR) measurements were made  
10 of samples 3b. The ESR measurements lead to the  
11 conclusion that the spins in the system are indeed  
12 interacting and the number of spins led us to the  
13 conclusion that the system was indeed ferromagnetic.  
14 Added to this, the occurrence of only one major peak  
15 with no hyperfine interactions indicates that the  
16 system is indeed pure and only the polymer is acting  
17 to give magnetism.

18

19 Figure 6 shows the low field behaviour of sample  
20 3b\_2. The intensity is much reduced and we are  
21 approaching the noise of the system. However the  
22 curve visible is indicative of insulating behaviour.  
23 Initially before the NMP has been driven off,  
24 PANiCNQ is conducting. The inventors assume there  
25 is a conduction pathway via the NMP as the Pani  
26 backbone still contains a quinoid ring. Although the  
27 observation of the conductivity is only qualitative,  
28 it is another piece of evidence showing how the  
29 system changes over time after the initial  
30 fabrication.

31

32

1 All documents referred to in this specification are  
2 herein incorporated by reference. Various  
3 modifications and variations to the described  
4 embodiments of the inventions will be apparent to  
5 those skilled in the art without departing from the  
6 scope and spirit of the invention. Although the  
7 invention has been described in connection with  
8 specific preferred embodiments, it should be  
9 understood that the invention as claimed should not  
10 be unduly limited to such specific embodiments.  
11 Indeed, various modifications of the described modes  
12 of carrying out the invention which are obvious to  
13 those skilled in the art are intended to be covered  
14 by the present invention.



## 1     Claims

2

3     1.   A substituted conjugated polymer comprising a  
4           conjugated polymer which is substituted with an  
5           organic electron acceptor.

6

7     2.   The substituted conjugated polymer according to  
8           claim 1 wherein the conjugated polymer  
9           comprises aromatic groups.

10

11    3.   The substituted conjugated polymer according to  
12           claim 2, wherein the conjugated polymer  
13           comprises heterocyclic aromatic groups  
14           containing a nitrogen atom in the ring  
15           structure.

16

17    4.   The substituted conjugated polymer according to  
18           any one of the preceding claims wherein the  
19           conjugated polymer comprises polyaniline,  
20           polypyridine, polypyrrole, polyparaphenylene,  
21           polyphenylene-vinylene (PPV), polythiophene or  
22           polyfluorene.

23

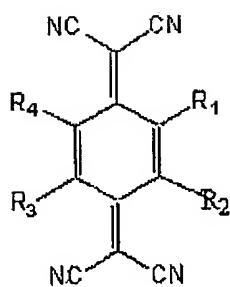
24    5.   The substituted conjugated polymer according to  
25           any one of the preceding claims wherein the  
26           conjugated polymer is polyaniline or is a  
27           polymer obtained from substituted aniline  
28           monomers.

29

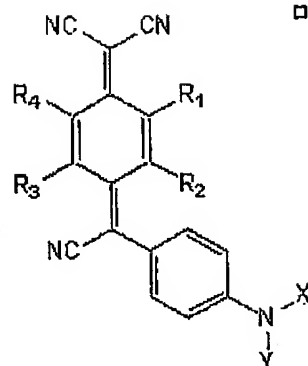
30    6.   The substituted conjugated polymer according to  
31           claim 5 wherein the polyaniline is emeraldine  
32           base polyaniline.

- 1     7.    The substituted conjugated polymer according to  
2            any one of the preceding claims wherein number  
3            average molecular weight of the conjugated  
4            polymer is in the range 4000 to 250 000 Dalton.  
5
- 6     8.    The substituted conjugated polymer according to  
7            any one of the preceding claims wherein the  
8            number average molecular weight of the  
9            conjugated polymer is greater than 19000  
10          Dalton.  
11
- 12    9.    The substituted conjugated polymer according to  
13            any one of the preceding claims wherein the  
14            electron acceptor comprises  
15            tetracyanoquinodimethane (TCNQ),  
16            tetracyanonapthoquinodimethane (TNAP),  
17            tetracyanoethylene (TCNE),  
18            dichlorodicyanobenzoquinone (DDQ), or a TCNQ  
19            derivative.  
20
- 21    10.   The substituted conjugated polymer according to  
22            claim 9 wherein the electron acceptor comprises  
23            a TCNQ derivative having formula I, formula II,

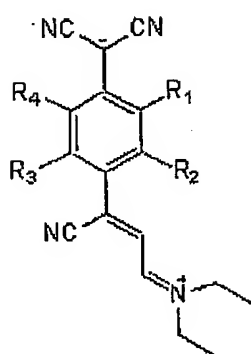
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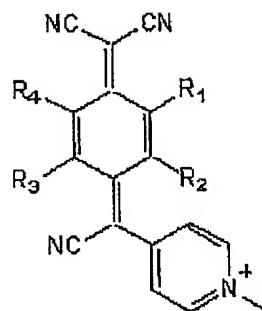
Formula I



Formula II



Formula III



Formula IV

1 where

2  $R_1 = R_2 = R_3 = R_4 = F, Me, Ph$  or  $NCH_2CH_3$ ; or

3  $R_2 = R_4 = H$  and  $R_1 = R_3 = I, Br, OMe, CN, PhCH_2$ , a

4  $C_1-C_8$  alkyl group (preferably hexyl, Me, Et or

5  $iPr$ ); or

6  $R_2 = R_4 = H$  and  $R_1 = OMe$  and  $R_3 = OEt, OiPr,$

7  $OiButyl, OiPentyl$ ; or

8  $R_2 = R_4 = H$  and  $R_1 = OEt$  and  $R_3 = SMe$ ; or

- 1            $R_2 = R_4 = H$  and  $R_3 = Me$  and  $R_1 = I, Br$  or  $Cl$ ; or  
2            $R_1 = R_2 = OCH_2CH_2O$  and  $R_3 = OMe$  and  $R_4 = H$ ; or  
3            $R_2 = R_4 = H$  and  $R_3 = Br$  and  $R_1 = OCH_2CH_2OH$ ; or  
4            $R_2 = R_3 = R_4 = H$  and  $R_1 = Me, Et, OMe, CO_2Me,$ ; and  
5            $X = Y = C_1-C_8$  alkyl group or  $CH_2CH_2OH$ ; or  $X = C_1-$   
6            $C_8$  alkyl group and  $Y = CH_2CH_2OH$   
7  
8       11. The substituted conjugated polymer according to  
9           claim 9 wherein the electron acceptor is  
10          tetracyanoquinonedimethane (TCNQ).  
11  
12       12. The substituted conjugated polymer according to  
13           any one of the preceding claims wherein the  
14           substituted conjugated polymer is polyaniline  
15           tricyanoquinonedimethane (PANiCNQ).  
16  
17       13. A ferromagnetic material comprising a  
18           substituted conjugated polymer according to any  
19           one of the preceding claims.  
20  
21       14. The ferromagnetic material according to claim  
22           13 wherein the ferromagnetic material is the  
23           substituted conjugated polymer according to any  
24           one of claims 1 to 12.  
25  
26       15. The ferromagnetic material according to claim  
27           13 or claim 14, wherein the material is  
28           ferromagnetic at room temperature.  
29  
30       16. The ferromagnetic material according to any one  
31           of claims 13 to 15 wherein the material is

- 1 ferromagnetic at temperatures above room  
2 temperature.  
3
- 4 17. The ferromagnetic material according to claim  
5 16 wherein the material is ferromagnetic up to  
6 500 K.  
7
- 8 18. The ferromagnetic material according to any one  
9 of claims 13 to 17 wherein the material has a  
10 mass magnetisation at room temperature of at  
11 least  $0.003 \text{ JT}^{-1}\text{Kg}^{-1}$ .  
12
- 13 19. The ferromagnetic material according to claim  
14 18 wherein the material has a mass  
15 magnetisation at room temperature of between  
16  $0.003$  and  $30 \text{ JT}^{-1}\text{Kg}^{-1}$ .  
17
- 18 20. A method for producing a ferromagnetic polymer  
19 which method comprises reacting a conjugated  
20 polymer with an organic electron acceptor.  
21
- 22 21. The method according to claim 20, wherein the  
23 method comprises the steps:  
24 a) dissolving the conjugated polymer in an  
25 appropriate solvent,  
26 b) adding the organic electron acceptor to  
27 the solution and refluxing the resultant  
28 solution for at least 24 hours,  
29 c) cooling and filtering the refluxed  
30 solution from step b and collecting and  
31 evaporating the filtrate to form a solid  
32 polymer,

- 1           d) drying the polymer from step c, and  
2           allowing the polymer to reach a steady  
3           ferromagnetic state.  
4
- 5       22. The method according to claim 21 wherein the  
6           molar ratio of conjugated polymer and organic  
7           electron acceptor in the mixture of step b is  
8           1:2.  
9
- 10       23. The method according to claim 21 or claim 22  
11           wherein the electron acceptor is  
12           tetracyanoquinonedimethane (TCNQ).  
13
- 14       24. The method according to any one of claims 21 to  
15           23, wherein the conjugated polymer is  
16           polyaniline or is a polymer obtained from  
17           substituted aniline monomers.

Fig 1

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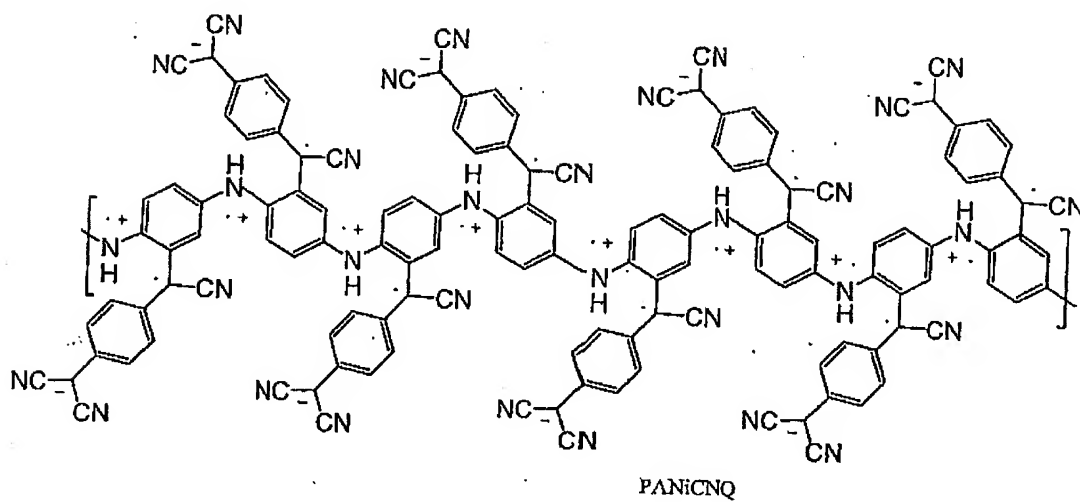
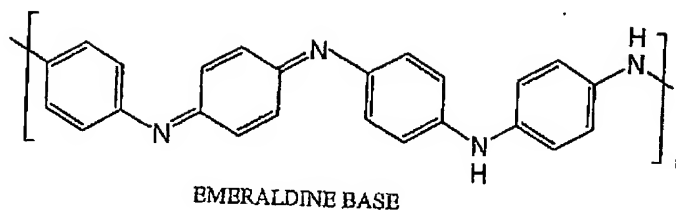
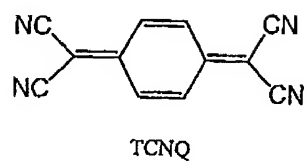
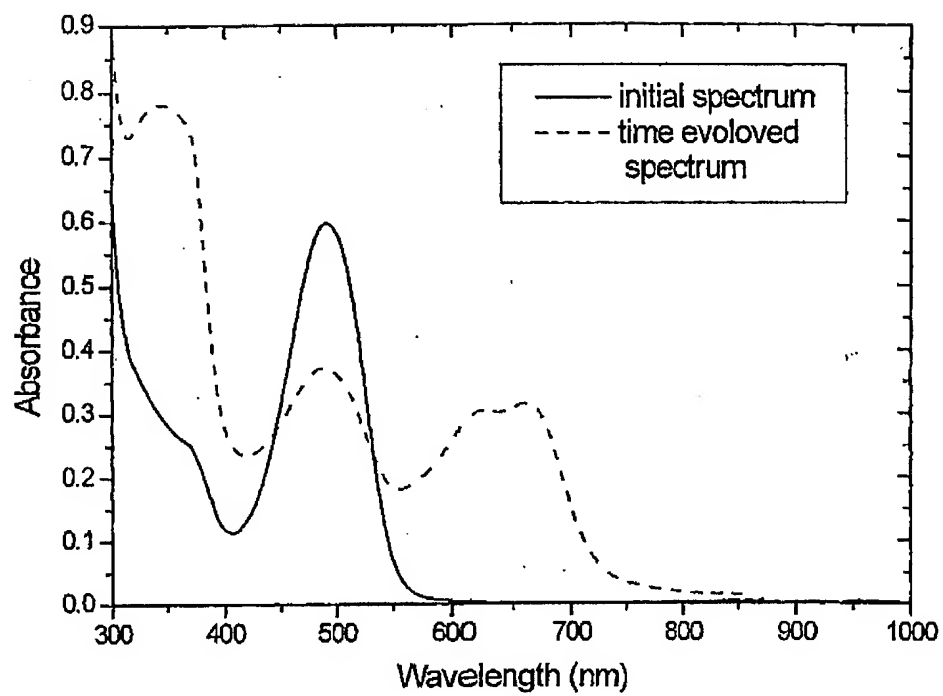


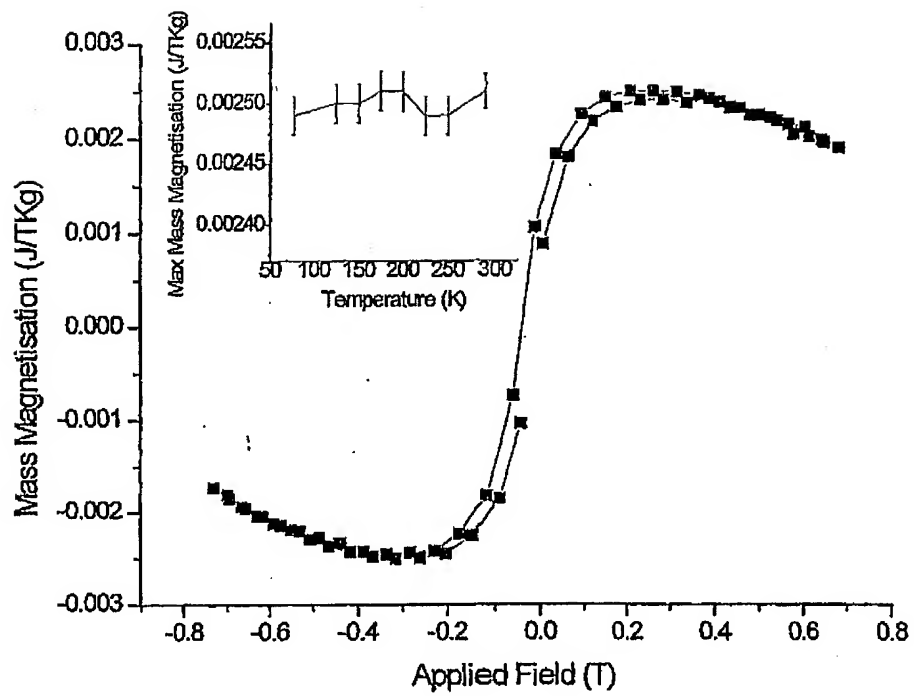
Fig 2





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Fig 3



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Figure 4a

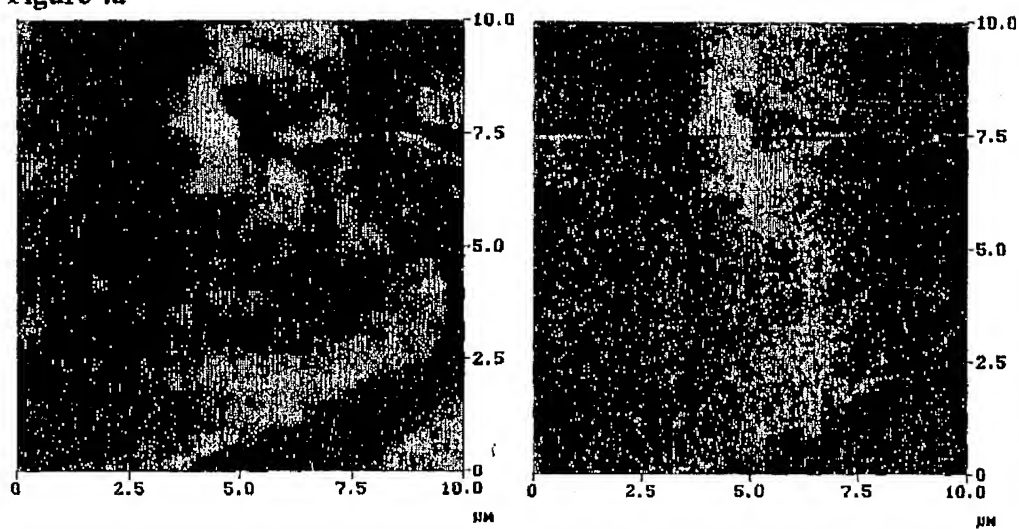
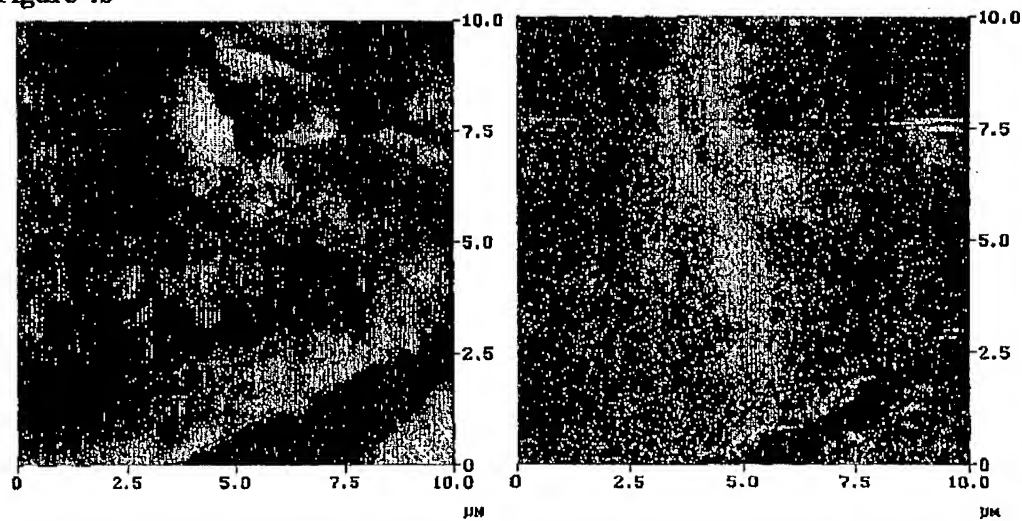


Figure 4b



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Figure 4c

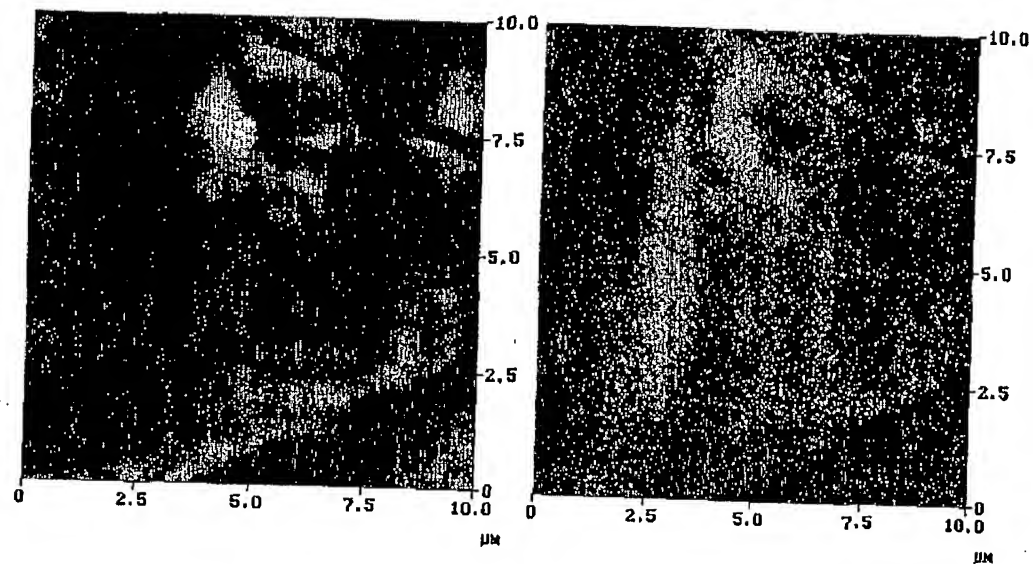
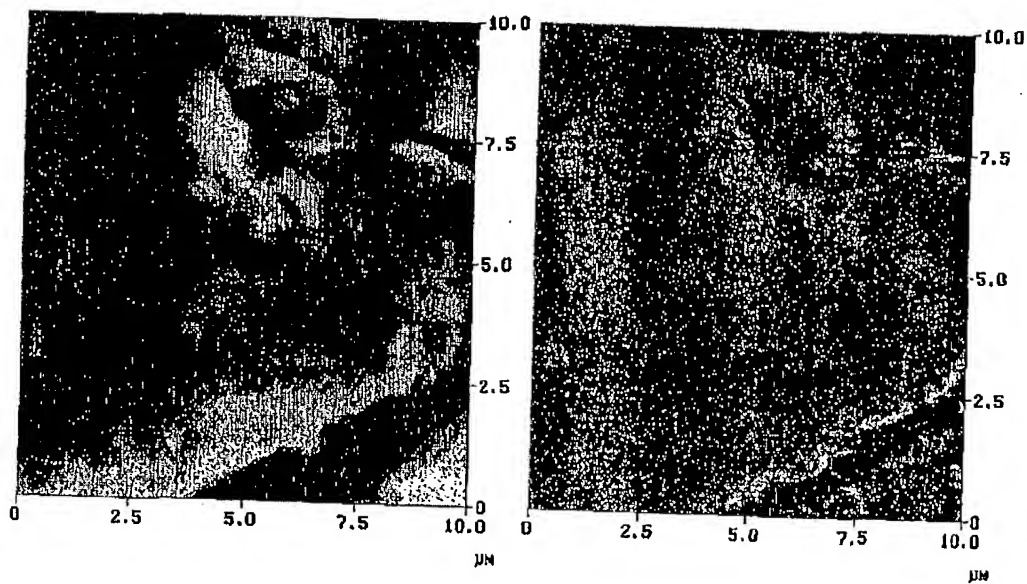
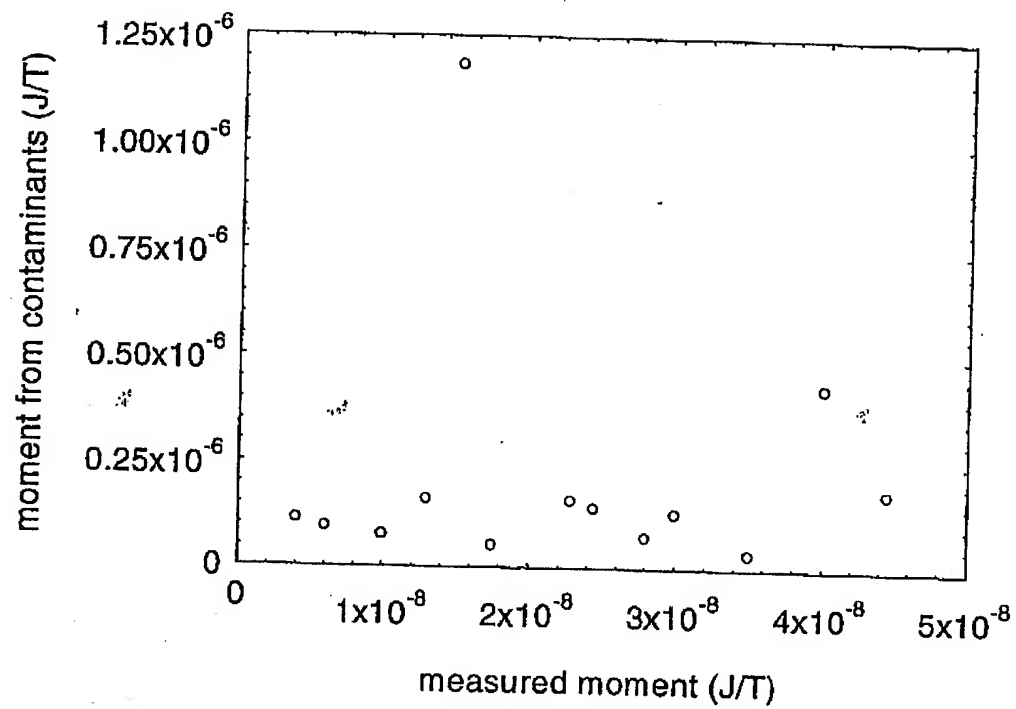


Figure 4d



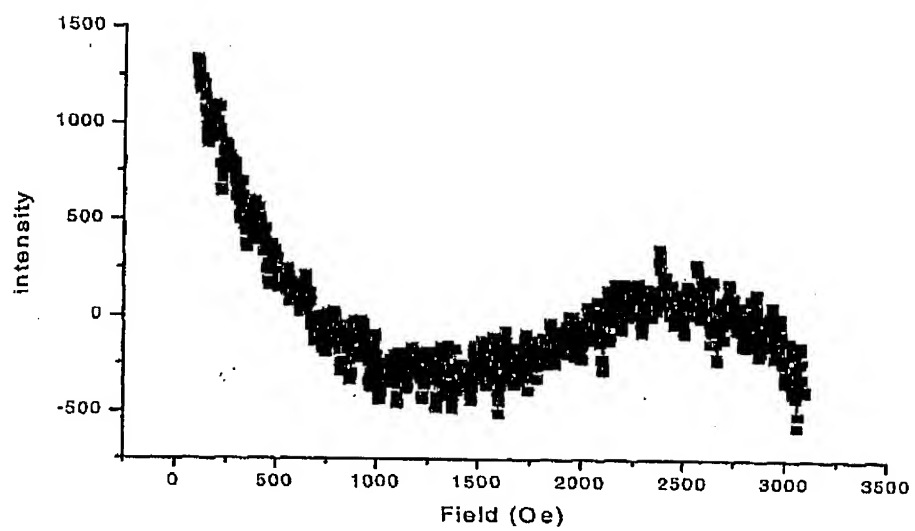
6/7

Figure 5



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Figure 6



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 03/00254

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08G73/02 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	DATABASE WPI Week 199348 Derwent Publications Ltd., London, GB; AN 1993-383154 XP002242867 & JP 05 287088 A (NIPPON SODA CO), 2 November 1993 (1993-11-02) abstract	1-4, 9-11
A	---	13-24
X	DATABASE WPI Week 199313 Derwent Publications Ltd., London, GB; AN 1993-105403 XP002242868 & JP 05 047211 A (RICOH KK), 26 February 1993 (1993-02-26) abstract	1-12
A	-----	13-24

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 5287088	A	02-11-1993	JP 3334111 B2	15-10-2002
JP 5047211	A	26-02-1993	NONE	